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(54) ELECTROLYTIC CAPACITOR

(71) We, INTERNATIONAL STANDARD ELECTRIC CORPORATION, a Corporation organised and existing under the laws of the State of Delaware, United States of America, of 320 Park Avenue, New York 22, State of New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to an electrolytic capacitor comprising at least one porous body or a porous layer of electrochemical valve metal arranged on a base and connected thereto.

Electrolytic capacitors have been known for a long time containing porous bodies of electrochemical valve metal for achieving a large electrical capacity, in which a dielectric layer of oxide is produced on the entire external and internal surface by way of electrical forming. The second coating of such capacitors is formed by either a liquid or solid electrolyte. The electrical connection to the porous body of electrochemical valve metal, such as aluminium, tantalum, niobium, etc., is established, as a rule, by a corresponding wire sintered into the body. It appears to be more difficult to produce the cathode connection which is aimed at establishing the electrical connection with either the solid or the liquid electrolyte. When using a liquid electrolyte, it is necessary to use a leak-proof container which is mostly made of metal, and itself represents the cathode terminal. The electrical terminal extending to the porous body of electrochemical valve metal must then be led out of the container in a leak-proof and electrically insulated manner. In the case of electrolytic capacitors employing a so-called solid electrolyte which mostly consists of a metal oxide, such as manganese dioxide, slightly emitting oxygen, the electrical connection is effected via a sequence of layers of carbon, conducting silver, and soldering metal. These layers are without exception very brittle, thus not only causing a danger of mechanical destruction but also that of a high contact or transfer resistance.

With respect to electrolytic capacitors employing a porous body of electrochemical valve metal, the porous body has also already been deposited on a base, or produced directly thereon by way of sintering. As the base there is used, as a rule, a sheet of metal of the same electrochemical valve metal as that from which the porous body is made. Such a metallic base then simultaneously forms the electrical connection to the electrochemical valve metal body. The electrical connection (terminal) extending to the solid electrolyte must then likewise be attached to the porous electrochemical valve metal body, by being insulated from the base.

It is an object of the present invention to improve electrolytic capacitors employing a porous body or a porous layer of electrochemical valve metal, in that the cathode terminal is electrically insulated from the porous body of electrochemical valve metal, but arranged to be connected thereto in a mechanically rigid manner.

According to the present invention there is provided an electrolytic capacitor comprising at least one porous body or a porous layer of electrochemical valve metal, arranged on a base and connected thereto, the base comprising a rigid porous body of a heat-resistant insulating material, as hereinafter defined.

For the purposes of this specification the term "heat-resistant insulating material" is to be understood to mean an insulating material that is not affected by heat during manufacture of the capacitor.

Such a porous body of heat-resistant insulating material is suitable for taking up in its pores and on its surface either a solid or liquid electrolyte. The cathode terminal may be arranged on a surface of this body of insulating material by being electrically insulated from the electrochemical valve

metal body. In spite of this, however, the body of electrochemical valve metal is mechanically connected in a rigid manner to the cathode terminal by the porous body of insulating material. From this results a mechanically good connection for the cathode of the capacitor, and also a very space saving and simple construction, so that a special housing (casing) may be omitted as a rule. Moreover, the cathode terminal is retained in a mechanically firm manner on the porous body of insulating material so that when using solid electrolytes, the danger of an increased contact (transfer) resistance or that the electrode layer may peel off, is minimised.

This also substantially improves the method of manufacturing such capacitors, because the sintered body of electrochemical valve metal, during its treatment for producing the sequence of layers, i.e. of the dielectric layer and the layer of the solid electrolyte, can be retained and easily handled by means of the body of insulating material. But also electrical capacitors employing a liquid electrolyte can be simplified substantially in this way, because the liquid electrolyte can be easily brought into the pores of the body of insulating material and because, apart from a protective envelope for the capacitor, there is not required a special capacitor casing.

The porous body of heat-resistant insulating material preferably has a porosity of at least 30%. Preferably, this body consists of ceramics or aluminium oxide.

The base of insulating material for the porous body of electrochemical valve metal may have various shapes.

For capacitors of particularly flat design it is specially suitable to provide a base having the shape of a plane plate. On one or on both opposite sides of this plate, several porous bodies or layers of electrochemical valve metal may be arranged, separated from one another. Following the manufacture of the capacitors, this plate may be subdivided into individual units, but in some cases it may be of advantage to leave several capacitors on one single base, for being electrically connected to one another in a desired way. When arranging two bodies or layers on one common base of insulating material, both are connected in such a way to one another either by the layer of solid electrolyte surrounding both, or by the liquid electrolyte as contained in the porous layer of insulating material, that there will result a bipolar capacitor unit.

The base of porous insulating material, however, may also have another shape. Thus, it may be designed to have the shape of a cylindrical elongated body, hence the shape of a rod which, subsequently to the manufacture of the various capacitor units, may likewise be subdivided into individual elements.

The cylindrical shape of the porous base of insulating material, however, may also be designed to have the shape of a tube, so that the porous body of electrochemical valve metal is positioned inside the tube, thus the base of insulating material will simultaneously form a mechanical envelope and a protection for the porous body of electrochemical valve metal.

In order to obtain a particularly large surface, the porous body of insulating material may be so designed as to comprise inward angles in its cross-sectional shape. Such a body, for example, would have a star-shaped cross-section. In this way it is possible to achieve a further enlargement of the surface by maintaining a small-size design.

The cathode connection, hence the terminal at the solid or liquid electrolyte, may be arranged on the base of porous insulating material in the form of a firmly adhering layer. It is of particular advantage, however, to provide a recess (depression) or a bore hole in the body of insulating material, into which there is inserted the cathode terminal in the form of a metal pin, metal wire, or sheet metal strip, thus still further improving the mechanical holding.

It is already known from the prior art to mechanically hold or to resiliently support the counter electrode in a depression or bore hole provided for in a sintered body of electrochemical valve metal (DT-AS 1,142,967). In the present case, however, the electrode is not retained in the sintered body of electrochemical valve metal, but in the base of porous insulating material.

Connection to the porous body of electrochemical valve metal is established in such a way that the body or the layer of valve metal is covered up at a suitable point before producing the dielectric oxide layer. Subsequently to the deposition or the production of the semiconducting layer representing the solid electrolyte, this cover is removed again, so that the valve metal is exposed at this point for permitting an electrical anode terminal to be attached thereto. The covering up may be carried out, for example, with the aid of a suitable setting (curing) insulating material which may be later on removed by way of grinding or peeling.

The capacitor may also be designed in such a way as to consist of a layer of porous electrochemical valve metal which is provided on both sides with a boundary of layers of a porous insulating material. In further developing this type of embodiment it is also possible to provide a multiple sequence of alternating layers of insulating

material and electrochemical valve metal. In these types of embodiment it is of advantage to arrange the cathode terminal on one face side of the layer sequence, with the electrochemical valve metal being exposed on this face side by way of grinding. In that case, however, care will have to be taken that the anode terminal is exclusively in contact with the layer of electrochemical valve metal, and not with the electrolyte as existing in the porous layer of insulating material. If necessary, a suitable insulating material will have to be brought at this point into the pores on the surface of the porous body of insulating material, in order thus to prevent the electrolyte from coming to the surface at this particular point.

The electrical contact with the layer of electrochemical valve metal and with the electrolyte on the surface of the body of insulating material, however, may also be established with the aid of suitable contact springs.

For protecting the capacitor after having been manufactured, it may be coated with a suitable insulating layer (coating, film) serving as a protective envelope. In the most simple way, this may be achieved by dipping the capacitor and a portion of the lead wires thereof into an insulating material which is first liquid and becomes hard later on.

According to another aspect of the present invention, the capacitor may be manufactured in such a way that the electrochemical valve metal powder is mixed with a suitable binder and deposited on to a rigid porous base of a heat-resistant insulating material, as hereinbefore defined, which is later on sintered to become a porous body or a porous layer.

It is also possible, however, to deposit the electrochemical valve metal powder as mixed with a binder, on to a not yet sintered body of the same material as that of the base, such as a ceramic raw material, and to sinter both in common to one another to form one continuous body.

This process, in the course of which the electrochemical valve metal powder and the material of the base are sintered in common, may be further embodied in such a way that the electrochemical valve metal powder as well as the raw material for the base, by adding a solvent or dispersion agent, as well as an organic polymer binder, are processed to become self-supporting layers, of which suitable portions are placed on top of each other and sintered to one another. The process of manufacturing capacitors from electrochemical valve metal powder by adding a polymer binder and a solvent or dispersion agent, is known per se from the German Offenlegungsschrift (DT-OS) 2,418,117.

When the rigid porous body of insulating material with the porous body of electrochemical valve metal as arranged thereon, or the porous layer of electrochemical valve metal is manufactured in accordance with one of these processes, there is carried out in the usual way an electrical forming in a suitable electrolyte for producing the dielectric oxide layer on the body of electrochemical valve metal. In the course of this, the electrolyte penetrates into pores of the porous body of insulating material and thus also reaches the body of electrochemical valve metal from that side on which it is placed on the base. Subsequently to the forming treatment, of course, the forming electrolyte has to be removed again from the pores of the body of insulating material unless it simultaneously serves as the operating electrolyte of the capacitor.

After having produced the dielectric oxide layer, the second coating is deposited on to the oxide layer in the form of a suitable electrolyte. To this end, the entire one-piece porous body is saturated with the electrolyte. When using liquid electrolytes it is of advantage for the layer or the body of electrochemical valve metal to be coated on both sides or on all sides by the rigid porous body of insulating material.

For producing a layer of solid electrolytes, for example, the arrangement may be dipped in the manner known per se, into an aqueous solution of manganese nitrate, and decomposed to form manganese dioxide by heating the manganese nitrate in the pores. There will then result a continuous layer of manganese dioxide on the internal as well as on the external surface of the porous bodies of electrochemical valve metal and of insulating material.

In the way described hereinbefore, the electrical contact with the electrolyte is established by means of a suitable conducting layer on the body of insulating material, or else by a conductor which is inserted into a depression or bore hole provided for in the body of insulating material.

Examples of capacitors according to the invention are schematically shown in Figures 1 to 3 of the accompanying drawings, in which:

Figure 1 shows a cross-section taken through a capacitor provided with a plate-shaped base of insulating material,

Figure 2 shows three different cross-sectional shapes of both the body of insulating material and the layer of electrochemical valve metal, and

Figure 3 shows a modified example of a

capacitor, both in a sectional and top view.

The sectionally shown capacitor according to Figure 1 consists of a plate-shaped base 1 of rigid porous insulating material on which a porous layer of electrochemical valve metal 2 is arranged. The valve metal electrode 4 is arranged in the form of a conducting layer on the layer 2 of electrochemical valve metal, i.e. at the point where this layer is not covered with a dielectric oxide layer and a semiconductor layer 3. The semiconductor electrode (cathode connection) 5 is arranged in the form of a conducting layer on the semiconductor layer 3, i.e. at the point where the latter directly rests on the porous base 1. For the sake of enabling a better understanding, the dielectric oxide layer has been omitted on the entire surface of the valve metal layer 2, and it is also not shown how the semiconductor layer 3 extends into the pores of the porous bodies 1 and 2. The lead wires 6 and 7 are attached to the electrodes 4 and 5. The entire capacitor is encapsulated by a suitable insulating compound 8.

Figure 2, by way of example, shows three different cross-sectional shapes relating to the rigid porous insulating base and the porous layer of electrochemical valve metal as arranged thereon. Figure 2a, in a cross-sectional view, shows a rod-shaped porous base 1 of insulating material which is surrounded by a jacket of a porous layer 2 of electrochemical valve metal.

In the type of embodiment as shown in Figure 2b, the porous base 1 of insulating material is designed to have the shape of a hollow cylinder which is filled with the porous body 2 of electrochemical valve metal. Figure 2c shows a type of embodiment in which the porous base 1 has a star-shaped cross-section, hence comprises inwardly extending angles, as is indicated by the reference numeral 9. In this way it is possible to obtain a particularly large surface of the base and, consequently, a large surface of the porous layer 2 of electrochemical valve metal requiring little space.

Figure 3, in a sectional and top view, shows an electrolytic capacitor according to the invention, in which the porous base 1 is designed to have the shape of a rectangular plate. Two porous layers of electrochemical valve metal 2a and 2b are arranged on the two surfaces of this plate lying opposite each other, and joined to one another by one common semiconductor layer 3. The dielectric oxide layer on both the inner and the outer surfaces of the electrochemical valve metal layers, and the portions of the semiconductor layer 3 as arranged inside the porous bodies 1, 2a and 2b. are not shown in this drawing. At exposed points of the layers 2a and 2b of electrochemical valve metal, there are arranged the electrodes 4a and 4b in the form of conducting layers, to which the lead wires 6a and 6b are attached. The plate of insulating material 1 is provided at 10 with a bore hole into which also the semiconductor layer 3 extends. This layer is contacted at this point by an inserted lead wire or rod 7a. The entire arrangement, of course, and as shown in Figure 1, may still be provided with a protective insulating envelope.

WHAT WE CLAIM IS:—

1. An electrolytic capacitor comprising at least one porous body or a porous layer of electrochemical valve metal, arranged on a base and connected thereto, the base comprising a rigid porous body of a heat-resistant insulating material, as hereinbefore defined.

2. A capacitor according to Claim 1, wherein the porosity of the base amounts to at least 30%.

3. A capacitor according to Claim 1 or 2, wherein the base consists of ceramics.

4. A capacitor according to Claim 1 or 2, wherein the base consists of aluminium oxide.

5. A capacitor according to one of Claims 1 to 4, wherein the base is a plane plate.

6. A capacitor according to one of Claims 1 to 4, wherein the base is a tube.

7. A capacitor according to Claim 6, wherein the tube is cylindrical.

8. A capacitor according to Claims 1 to 4, wherein the base comprises a body whose cross-section has inwardly extending angular depressions.

9. A capacitor according to Claims 1 to 8, wherein several porous bodies or layers of electrochemical valve metal which are separated from one another, are arranged on the base.

10. A capacitor according to Claim 9, wherein porous bodies or layers of electrochemical valve metal which are separated from one another, are arranged next to each other on the same surface of the base.

11. A capacitor according to Claim 9, wherein porous bodies or layers of electrochemical valve metal which are separated from one another, are arranged on sides of the base lying opposite each other.

12. A capacitor according to any one of Claims 1 to 11, wherein a dielectric oxide layer is formed on both the inside and the outside surface of either the porous sintered body or the layer of electrochemical valve metal, and that a layer of a semiconducting oxide is arranged

on the oxide layer and on the inside and outside surface of the base.

13. A capacitor according to Claim 12, wherein the base is provided with at least one depression or bore hole in which an electrode terminal is arranged.

14. A capacitor according to any of Claims 1 to 13, wherein a porous body 2 of electrochemical valve metal or a porous layer of electrochemical valve metal is arranged between two rigid porous base layers of insulating material.

15. A capacitor according to any of Claims 1 to 13, wherein several porous layers of electrochemical valve metal and rigid porous base layers of insulating material are alternatingly arranged on top of each other.

16. A capacitor according to Claims 14 and 15, wherein the porous layer of electrochemical valve metal is contacted on a face side of the laminate.

17. A capacitor according to any of Claims 1 to 16, wherein the base is coated with an insulating material at least within the region of the porous body or the layer of electrochemical valve metal arranged thereon.

18. A process of manufacturing electrical capacitors according to any of Claims 1 to 17, wherein the electrochemical valve metal powder, mixed with a binder, is deposited on to a rigid porous base of heat-resistant insulating material, as hereinbefore defined, and, thereafter, sintered to form the porous body or porous layer respectively.

19. A process of manufacturing electrical capacitors according to Claims 1 to 17, wherein the electrochemical valve metal powder, mixed with a binder, is deposited on to a body of raw ceramic material, and both together are sintered to form agglomerated porous bodies.

20. A process according to Claim 19, wherein the electrochemical valve metal powder as well as the raw material for the ceramic base, are processed by adding a solvent or dispersion agent as well as an organic polymer binder, to form self-supporting layers of which suitable portions are placed on top of each other and sintered with one another.

21. A process according to Claims 18 to 20, wherein larger, one-piece bodies are manufactured, with the latter being divided into individual units either prior to or after the sintering.

22. A process according to Claims 18 to 21, wherein subsequently to the sintering, portions of the porous bodies or layers of electrochemical valve metal are masked with this masking being removed after having produced both the dielectric oxide layer and the semiconducting oxide layer, with the electrochemical valve metal being contacted at this point thereafter.

23. A process according to Claim 22, wherein following the production of the semiconducting layer on the dielectric oxide layer of the porous body of electrochemical valve metal and on the entire surface of the porous base, contacting layers are arranged on the semiconducting oxide layer at the points where they are directly placed on to the porous base.

24. A capacitor substantially as hereinbefore described with reference to and as illustrated in Figures 1 and 2 or Figure 3 of the accompanying drawing.

25. A method of making a capacitor substantially as hereinbefore described with reference to the accompanying drawing.

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1540332 COMPLETE SPECIFICATION

1 SHEET This drawing is a reproduction of the Original on a reduced scale

Fig. 1.

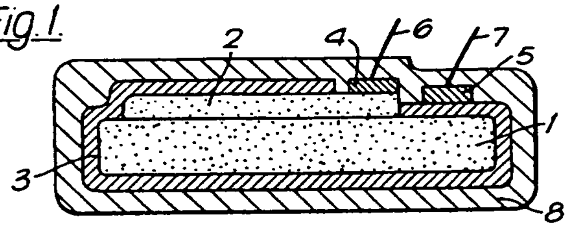

Fig. 2.

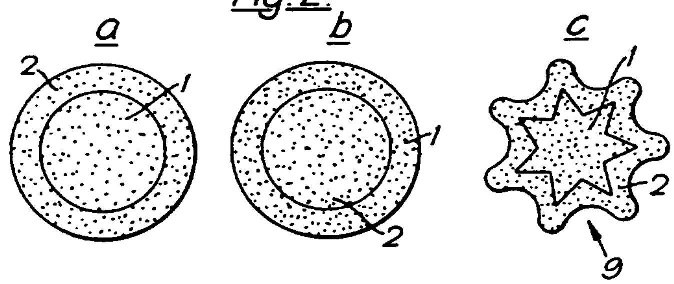

Fig. 3.